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Crystal Structures of $(AsPh_4)[TcO(SCOCOS)_2]$ and $(AsPh_4)_2[TcN(SCOCOS)_2]$. A Comparison of the Tc^VO^{3+} and Tc^VN^{2+} Cores in the Same Coordination Environment

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Abstract

The reaction of potassium dithiooxalate in acetone with $(AsPh_4)[TcNCl_4]$ in acetonitrile yields crystals of $(AsPh_4)_2[TcN(SCOCOS)_2]$ (**1**). We now report the X-ray structures of **1** and the oxo analogue $(AsPh_4)[TcO(SCOCOS)_2]$ (**2**), both of which contain the technetium atom in the +5 oxidation state and in the same coordination environment. Crystals of **1** and **2** belong to the triclinic space group $P\bar{1}$ with $Z = 2$. Unit cell parameters are: **1**, $a = 14.225(5)$, $b = 17.778(2)$, $c = 10.993(3)$ Å, $\alpha = 101.52(2)$, $\beta = 111.74(2)$, $\gamma = 100.68(2)°$ and **2**, $a = 12.294(2)$, $b = 12.531(2)$, $c = 13.071(2)$ Å, $\alpha = 115.10(1)$, $\beta = 114.22(1)$, $\gamma = 101.93(1)°$. Refinement with data measured with Cu Kα radiation converged at $R = 0.055$ for 7569 observed data **1** and at $R = 0.041$ for 4739 observed data **2**. The technetium atoms in the complex anions are five-coordinate with the four sulphur atoms in the basal position and either the oxygen or nitrogen in the apical position, to give a distorted square-pyramidal environment about each technetium. The Tc=O and Tc≡N bond lengths are 1.646(4) and 1.613(4) Å in **1** and **2** respectively.

Introduction

Technetium complexes containing the TcO^{3+} core are well known and a number have been characterised by X-ray diffraction studies [1, 2]. More recently, it has been shown that complexes containing the TcN^{3+} or TcN^{2+} cores are readily prepared by substitution reactions of $[TcNCl_2(PPh_3)_2]$ [3–5] and in particular of $[TcNCl_4]^-$ [6], generally with the reduction of Tc^{VI} to Tc^V in the latter case. The nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}), and being a powerful π-electron donor tends to stabilise transition metals in high oxidation states.

It is of interest to compare the structural effects of the Tc^VO^{3+} and Tc^VN^{2+} cores in the same coordination environment. To date, the only comparison that has been made is between the structures of $[N(PPh_3)_2][TcOCl_4]$ [7] and $(AsPh_4)[TcNCl_4]$ [8] which contain the Tc^VO^{3+} and $Tc^{VI}N^{3+}$ cores respectively. However, these complexes have the Tc atom in different oxidation states and the $N(PPh_3)_2^+$ cation appears to cause distortions from ideal geometry in the $[TcOCl_4]^-$ ion. We have prepared $(AsPh_4)_2[TcN(dto)_2]$ (**1**) (dto = dithiooxalate) and now report the structure **1** and the oxo analogue $(AsPh_4)[TcO(dto)_2]$ (**2**) [9], both of which contain the technetium in the +5 oxidation state.

Experimental

Ammonium [^{99}Tc]pertechnetate (31.7 mg Tc cm^{-3} in 0.1 mol dm^{-3} NH_3 solution) was supplied by Amersham International plc. The IR spectrum was determined for a KBr disc on a Perkin-Elmer 197 spectrophotometer. The microanalysis was performed by the Australian Microanalytical Service, Melbourne. Tetraphenylarsonium tetrachloronitridotechnetate(VI) was prepared according to the method of Baldas *et al.* [6], and tetraphenylarsonium bis(1,2-dithiooxalato)oxotechnetate(V) was prepared by a modification of the method of Davison *et al.* for the preparation of $(NBu_4)[TcO(dto)_2]$ [9].

Preparation of $(AsPh_4)_2[TcN(dto)_2]$

Potassium dithiooxalate (250 mg, 1.26 mmol) dissolved in acetone:water (1:3) was added to a solution of $(AsPh_4)[TcNCl_4]$ (138 mg, 0.216 mmol) in acetonitrile (3 cm^3). The mixture immediately turned a deep purple. $AsPh_4Cl$ (90 mg, 0.215 mmol) dissolved in water (1 cm^3) was added and the solution allowed to stand at room temperature. A pale purple microcrystalline product slowly formed and was collected by filtration, washed with a small amount of cold ethanol, and dried; (yield 200 mg, 83% based on $(AsPh_4)[TcNCl_4]$). Melting point

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(m.p.) decomp. *ca.* 215 °C. *Anal.* Found: C, 56.1; H, 3.7; N, 1.1; S, 11.2. Calc. for $C_{52}H_{40}As_2NO_4S_4Tc$: C, 55.77; H, 3.60; N, 1.25; S, 11.45%. The IR spectrum showed peaks at 1612vs, 1438s, 1079m, 1071m (Tc≡N), 1039s, 742s, 735s, 685s cm^{-1}.

X-ray Data Collection and Structure Analyses

Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of an acetonitrile–ethanol solution (3:1, v/v) of $(AsPh_4)_2[TcN(dto)_2]$ (**1**) and of $(AsPh_4)[TcO(dto)_2]$ (**2**). Accurate unit cell parameters were determined at 16 °C by least-squares fits of 2θ values measured with Cu Kα radiation for 25 independent reflections well separated in reciprocal space. Integrated intensities were measured on a Rigaku-AFC four-circle diffractometer with Cu Kα radiation (graphite-crystal monochromator, $\lambda = 1.5418$ Å) and recorded by an ω–2θ scan with 10 s stationary background counts to a maximum $\sin\theta/\lambda = 0.588$ Å^{-1}. The intensities were corrected for Lorentz and polarisation effects and for absorption.

The sites of the Tc, As and most of the non-hydrogen atoms were determined by a combined Patterson/structure expansion method using SHELXS-86 [10]. Subsequent difference syntheses revealed the sites of all the remaining non-hydrogen atoms. Because of the many parameters, H atoms for **1** were not included in the analysis, whereas for **2** they were included at idealised positions. The structures were refined by full-matrix least-squares procedures; the function minimised was $\Sigma w(\Delta F)^2$, where $\Delta F = (|F_o| - |F_c|)$, with the terms weighted according to $w = (\sigma^2|F_o| + m|F_o|^2)^{-1}$ for which $m = 8 \times 10^{-4}$ (**1**) and 2×10^{-4} (**2**). During the refinements a number of intense low order reflections which showed severe extinction were omitted from the final refinement cycles, *viz.* 020, 101, 041, $\bar{1}02$, 112, $\bar{1}22$ (**1**) and $0\bar{3}1$, $1\bar{3}1$, 001, 121, $\bar{1}\bar{1}2$, 102, $\bar{2}\bar{1}5$ (**2**). The R indices were defined as $R = \Sigma\Delta F/\Sigma|F_o|$, $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$ and the 'goodness of fit' given by $G.O.F. = [\Sigma w(\Delta F)^2(n - m)]^{1/2}$ where n is the number of reflections used in the refinement and m is the number of variables.

The crystal data, data collections and refinements are summarised in Table I.

Final atomic positional parameters of the non-hydrogen atoms are given in Tables II and III for **1** and **2** respectively. Complex neutral scattering factors were given to the non-hydrogen atoms [11],

TABLE I. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement of **1** and **2**

	$(AsPh_4)_2[TcN(dto)_2]$	$(AsPh_4)[TcO(dto)_2]$
Formula	$C_{52}H_{40}As_2NO_4S_4Tc$	$C_{28}H_{20}AsO_5S_4Tc$
Formula weight	1119.89	738.53
Crystal dimensions (mm)	0.4 × 0.4 × 0.1	0.40 × 0.35 × 0.13
Crystal colour	purple	red–brown
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	14.225(5)	12.294(2)
b (Å)	17.778(2)	12.531(2)
c (Å)	10.993(3)	13.071(2)
α (°)	101.52(2)	115.10(1)
β (°)	111.74(2)	114.22(1)
γ (°)	100.68(2)	101.93(1)
Cell volume (Å^3)	2425(3)	1476(1)
Molecules/cell	2	2
F(000)	1128	736
μ(Cu Kα) (cm^{-1})	56.24	78.23
Temperature (°C)	15(1)	15(1)
Wavelength (Å)	1.5418	1.5418
Absorption correction factors	1.71–5.83	2.17–9.42
2θ(max) (°)	130	130
Diffractometer	Rigaku-AFC	Rigaku-AFC
Scan rate (Δw) (°min^{-1})	4	4
Scan range (°)	$1.2 + 0.5 \tan\theta$	$1.2 + 0.5 \tan\theta$
Unique non-zero data used	7575	4746
Terms used for refinement	7569	4739
Final no. parameters refined	577	372
R	0.055	0.041
R_w	0.076	0.054
G.O.F. for last cycle	2.12	2.91
Residual density (e Å^{-3})	+0.84 and −1.55	+0.86 and −1.33
Max Δ/for last cycle	0.01	0.02

TABLE II. Fractional Coordinates for $(AsPh_4)_2[TcN(dto)_2]$

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
Tc	2738(1)	2463(1)	2015(1)
As(1)	9564(1)	1717(1)	-5271(1)
As(2)	6767(1)	3196(1)	-1129(1)
S(1)	4184(1)	2278(1)	1493(1)
S(2)	3224(1)	1661(1)	3505(2)
S(3)	3089(1)	3727(1)	1589(2)
S(4)	2135(1)	3095(1)	3599(2)
O(1)	5651(3)	1629(3)	2621(5)
O(2)	4699(4)	956(3)	3999(5)
O(3)	2147(4)	4825(3)	1887(6)
O(4)	1630(6)	4418(4)	3832(11)
N(1)	1691(4)	1892(3)	696(6)
C(1)	4807(4)	1741(3)	2527(5)
C(2)	4311(4)	1404(3)	3401(5)
C(3)	2367(5)	4248(3)	2210(8)
C(4)	2015(6)	3989(4)	3288(10)
C(5)	9311(4)	2727(3)	-5389(5)
C(6)	9068(5)	3154(3)	-4390(6)
C(7)	8895(6)	3895(4)	-4451(8)
C(8)	8904(6)	4160(4)	-5549(9)
C(9)	9116(8)	3732(5)	-6545(9)
C(10)	9335(6)	2996(4)	-6467(6)
C(11)	9155(4)	1013(3)	-7062(5)
C(12)	9764(4)	1176(3)	-7774(5)
C(13)	9427(5)	665(3)	-9104(6)
C(14)	8546(6)	12(3)	-9659(6)
C(15)	7961(6)	-148(4)	-8929(6)
C(16)	8283(5)	357(3)	-7598(6)
C(17)	8752(4)	1246(3)	-4440(5)
C(18)	9206(4)	878(3)	-3460(5)
C(19)	8577(5)	497(3)	-2901(6)
C(20)	7559(5)	512(3)	-3271(6)
C(21)	7098(4)	883(3)	-4263(6)
C(22)	7694(4)	1255(3)	-4851(6)
C(23)	11011(4)	1850(3)	-4154(5)
C(24)	11518(5)	1325(4)	-4541(6)
C(25)	12551(5)	1387(5)	-3638(6)
C(26)	13060(5)	1971(5)	-2400(6)
C(27)	12546(6)	2489(6)	-2015(6)
C(28)	11510(5)	2442(4)	-2905(6)
C(29)	6161(4)	3459(3)	-2796(5)
C(30)	6514(4)	3255(3)	-3801(5)
C(31)	6113(5)	3483(4)	-4982(5)
C(32)	5380(5)	3901(4)	-5151(6)
C(33)	5028(5)	4118(4)	-4144(6)
C(34)	5441(4)	3893(4)	-2922(6)
C(35)	6755(4)	3985(3)	331(5)
C(36)	5930(6)	3868(4)	709(8)
C(37)	5964(6)	4466(5)	1772(9)
C(38)	6769(6)	5158(5)	2393(6)
C(39)	7576(6)	5266(5)	2027(10)
C(40)	7576(6)	4671(4)	985(10)
C(41)	8171(4)	3182(3)	-833(5)
C(42)	8818(4)	3811(3)	-950(6)
C(43)	9853(4)	3790(4)	-772(6)
C(44)	10178(4)	3128(4)	-475(6)
C(45)	9524(5)	2516(4)	-362(6)
C(46)	8492(5)	2526(3)	-540(6)
C(47)	6008(4)	2138(3)	-1322(6)
C(48)	6117(6)	1890(3)	-167(6)
C(49)	5648(6)	1084(4)	-368(9)
C(50)	5120(6)	558(4)	-1690(8)
C(51)	5012(5)	822(3)	-2798(6)
C(52)	5459(4)	1621(3)	-2629(6)

TABLE III. Fractional Coordinates for $(AsPh_4)[TcO(dto)_2]$

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
Tc	747(1)	3039(1)	4776(1)
As	-2239(1)	534(1)	-3248(1)
S(1)	862(1)	4136(1)	6799(1)
S(2)	3026(1)	4484(1)	6054(1)
S(3)	-1350(1)	2994(1)	3877(1)
S(4)	836(1)	3308(1)	3151(1)
O(1)	2947(5)	5262(5)	9251(4)
O(2)	4783(4)	5724(4)	8654(4)
O(3)	-3025(4)	2227(5)	1376(4)
O(4)	-1187(5)	2405(5)	744(4)
O(5)	533(3)	1536(3)	4346(3)
C(1)	2569(5)	4895(5)	8107(4)
C(2)	3604(5)	5109(5)	7764(5)
C(3)	-1888(5)	2569(5)	2223(5)
C(4)	-843(5)	2701(5)	1872(4)
C(5)	-2791(4)	-517(4)	-5102(4)
C(6)	-4046(4)	-1618(4)	-6074(4)
C(7)	-4461(4)	-2336(5)	-7439(4)
C(8)	-3649(5)	-1934(5)	-7814(4)
C(9)	-2391(5)	-824(5)	-6830(5)
C(10)	-1965(4)	-117(4)	-5477(4)
C(11)	-409(4)	1053(4)	-1978(3)
C(12)	598(4)	2183(4)	-1576(4)
C(13)	1930(4)	2607(4)	-622(4)
C(14)	2250(4)	1886(5)	-90(4)
C(15)	1260(5)	760(5)	-487(5)
C(16)	-91(4)	330(4)	-1427(4)
C(17)	-3372(4)	-456(4)	-2981(4)
C(18)	-3950(4)	113(5)	-2332(5)
C(19)	-4744(5)	-629(6)	-2121(5)
C(20)	-4935(5)	-1893(6)	-2548(5)
C(21)	-4360(5)	-2471(5)	-3202(5)
C(22)	-3563(5)	-1749(4)	-3414(4)
C(23)	-2320(4)	2149(4)	-2887(4)
C(24)	-1857(4)	3132(4)	-1560(4)
C(25)	-1831(5)	4336(4)	-1263(5)
C(26)	-2241(5)	4575(5)	-2274(5)
C(27)	-2685(5)	3591(5)	-3585(5)
C(28)	-2742(4)	2370(4)	-3906(4)

and the hydrogen scattering factors were taken from ref. 12. Figures 1 and 2 have been prepared from the output of ORTEP [13]. The major calculations were performed on a VAX11/780 and DATA GENERAL Computer. See also 'Supplementary Material'.

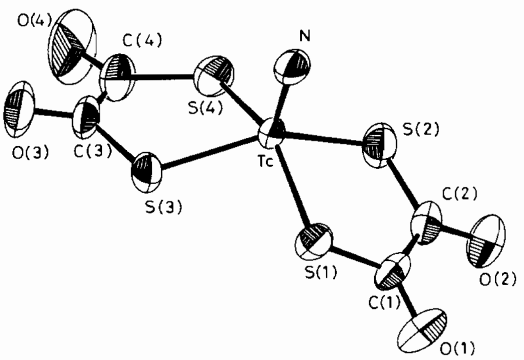

Fig. 1. A perspective view of the $[TcN(dto)_2]^{2-}$ anion in $(AsPh_4)_2[TcN(dto)_2]$ showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

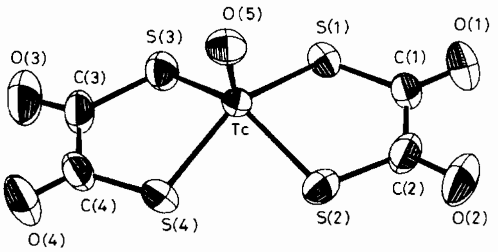

Fig. 2. A perspective view of the $[TcO(dto)_2]^-$ anion in $(AsPh_4)[TcO(dto)_2]$ showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Results and Discussion

Many technetium complexes containing the TcO^{3+} core have been prepared either by substitution reactions of $[Tc^{V}OCl_4]^-$ or by the reduction of TcO_4^- in the presence of coordinating ligands [1]. Similarly, substitution reactions of $[Tc^{VI}NCl_4]^-$, generally with the reduction of Tc^{VI} to Tc^{V}, have provided a convenient method for the formation of technetium complexes containing the Tc≡N group [6].

Recently, we have investigated substitution reactions of $[Tc^{V}OCl_4]^-$ and $[Tc^{VI}NCl_4]^-$ with benzene-1,2-dithiol ($bdtH_2$), oxalic acid (oxH_2) and K_2dto, with the aim of preparing complexes containing the $Tc^{V}{\equiv}N^{2+}$ and $Tc^{V}{=}O^{3+}$ cores in the same coordination environment. The five-coordinate complex, $(AsPh_4)[TcO(bdt)_2]$, was readily prepared and the anion exhibits square pyramidal geometry typical for this type of coordination [14]. However, attempts to prepare the nitrido analogue resulted in the formation of $(AsPh_4)[Tc^{V}(bdt)_3]$ [15]. This reaction, involving the removal of the nitrido atom from $[TcNCl_4]^-$ was surprising since it had been shown that the Tc≡N bond in such complexes is exceptionally stable [6, 8]. Similarly, substitution reactions involving oxalic acid failed to give the expected products but resulted in the novel complexes $(AsPh_4)_2[Tc^{V}O(ox)_2(C_2O_4H)]\cdot 3H_2O$ and $(AsPh_4)_4[Tc^{VI}{}_4N_4(O)_2(ox)_6]$ [16]. In contrast with the above reactions, $(AsPh_4)_2[Tc^{V}N(dto)_2]$ (**1**) was readily prepared in good yield. The X-ray structures of **1** and the oxo analogue $(AsPh_4)[Tc^{V}O(dto)_2]$ (**2**) now allow a direct structural comparison of the $Tc^{V}{\equiv}N^{2+}$ and $Tc^{V}{=}O^{3+}$ cores in the same coordination environment.

Molecular Structure of $(AsPh_4)_2[TcN(dto)_2]$ and $(AsPh_4)[TcO(dto)_2]$

The crystal structures of **1** and **2** consist of discrete $AsPh_4^+$ cations and $[TcN(dto)_2]^{2-}$ and $[TcO(dto)_2]^-$ anions respectively. Perspective views of the anions which include the atom numbering are shown in Figs. 1 and 2, and selected interatomic distances and angles are given in Tables IV and V.

TABLE IV. Selected Interatomic Distances (Å) and Angles (°) in the Coordination Sphere for $[TcN(dto)_2]^{2-}$

Tc–S(1)	2.391(2)	Tc–S(2)	2.378(2)
Tc–S(3)	2.387(2)	Tc–S(4)	2.390(2)
Tc–N(1)	1.613(4)	S(1)–C(1)	1.729(6)
S(2)–C(2)	1.728(6)	S(3)–C(3)	1.732(8)
S(4)–C(4)	1.717(8)	O(1)–C(1)	1.223(8)
O(2)–C(2)	1.214(8)	O(3)–C(3)	1.208(9)
O(4)–C(4)	1.206(15)	C(1)–C(2)	1.535(9)
C(3)–C(4)	1.562(15)		
S(1)–Tc–S(2)	86.2(1)	S(1)–Tc–S(3)	85.8(1)
S(1)–Tc–S(4)	148.6(1)	S(1)–Tc–N(1)	105.4(2)
S(2)–Tc–S(3)	148.4(2)	S(2)–Tc–S(4)	85.1(1)
S(2)–Tc–N(1)	105.5(2)	S(3)–Tc–S(4)	86.1(1)
S(3)–Tc–N(1)	106.1(3)	S(4)–Tc–N(1)	106.0(3)

TABLE V. Selected Interatomic Distances (Å) and Angles (°) in the Coordination Sphere for $[TcO(dto)_2]^-$

Tc–S(1)	2.330(1)	Tc–S(2)	2.327(1)
Tc–S(3)	2.330(1)	Tc–S(4)	2.328(2)
Tc–O(5)	1.646(4)	S(1)–C(1)	1.756(5)
S(2)–C(2)	1.759(6)	S(3)–C(3)	1.761(7)
S(4)–C(4)	1.754(5)	O(1)–C(1)	1.192(7)
O(2)–C(2)	1.201(6)	O(3)–C(3)	1.201(7)
O(4)–C(4)	1.204(7)	C(1)–C(2)	1.523(10)
C(3)–C(4)	1.532(10)		
S(1)–Tc–S(2)	86.7(1)	S(1)–Tc–S(3)	81.5(1)
S(1)–Tc–S(4)	142.7(1)	S(1)–Tc–O(5)	108.6(2)
S(2)–Tc–S(3)	141.3(1)	S(2)–Tc–S(4)	80.5(1)
S(2)–Tc–O(5)	109.9(2)	S(3)–Tc–S(4)	86.8(1)
S(3)–Tc–O(5)	108.8(2)	S(4)–Tc–O(5)	108.7(2)

Both complex anions have *pseudo*-C_{2v} symmetry and the technetium atoms are five-coordinate. As expected, the geometry about each technetium atom is distorted square pyramidal with the oxygen or nitrogen occupying the apical position. The distortions arise from the large *trans*-influence of the oxo [17] and nitrido [18] ligand and are manifested by the displacement of the technetium atoms from the basal plane by 0.647 and 0.759 Å for **1** and **2** respectively. The paucity of structural data for Tc$\equiv$N complexes containing sulphur ligands, and indeed of technetium nitrido complexes, allows only very general comparisons with **1**. The Tc$\equiv$N bond distances have been found to fall within two ranges *viz:* 1.581(5)–1.596(6) Å for $[\mathrm{Tc^{VI}NX_4}]^-$ (X = Cl, or Br) [8, 19], and 1.60(2)–1.64(2) Å for Tc$\equiv$N complexes containing N, S or P ligands [4, 6, 16, 20]. The Tc$\equiv$N bond length of 1.613(4) Å in **1** is similar to that observed for complexes in the latter range. The Tc–S bond distances of 2.378(2)–2.391(2) Å are similar to those observed for this bond in the only two other examples containing the nitrido group and sulphur ligands; $[\mathrm{TcN(S_2CNEt_2)_2}]$, 2.392(2)–2.405(2) Å [20], and $[\mathrm{TcN(C_9H_6NS)_2}]$ ($\mathrm{C_9H_6NSH}$ = 8-quinolinethiol) 2.3559(7) Å [6].

In contrast to the small number of technetium nitrido complexes structurally characterised, complexes containing the Tc=O group or $\mathrm{TcOS_4}$ core have been extensively studied by X-ray diffraction [2]. The Tc=O and Tc–S bond distances of 1.646(4) and 2.329(1) Å found for **2** are consistent with those observed in $[\mathrm{TcO(SCH_2CH_2S)_2}]^-$ and $[\mathrm{TcO(SCH_2COS)_2}]^-$ anions [21].

Included in Table VI are selected dimensions of the coordination sphere for a number of complexes of the type $[\mathrm{MX(L_4)}]^{n-}$ or $[\mathrm{MX(L{-}L)_2}]^{n-}$ (X = O, or N) which contain the metal atom in a similar coordination environment, and which have been structurally characterised by X-ray crystallography. Although oxo and nitrido complexes of transition metals have been extensively studied [22, 18], we are unaware of any oxo and nitrido complexes which contain the metal atom in the same oxidation state and coordination environment apart from those reported here.

An examination of the structural parameters for some $[\mathrm{MX(L)_4}]^{n-}$ or $[\mathrm{MX(L{-}L)_2}]^{n-}$ complexes listed in Table VI allows for some general observations. The M$\equiv$N bond lengths are significantly shorter than the analogous M=O distances (although there are large e.s.d.s quoted for the M–X lengths of Re and Mo complexes) indicative of a stronger π-interaction with the metal atom than in the oxo complexes. Consequently, this strong π-interaction would be expected to cause a lengthening of the M–L bonds in the nitrido complexes compared to those in the oxo analogues, and in fact this is generally observed. Recently, a study of the equilibrium $[\mathrm{TcXCl_4}]^- + \mathrm{Cl^-} \rightleftharpoons [\mathrm{TcXCl_5}]^{2-}$ (X = O or N) in non-aqueous and concentrated aqueous acid solutions has been reported [23, 24]. Although this equilibrium is clearly established for the oxo complex [23], there is no evidence that the analogous pentachloronitridotechnetate ion exists in solution [24]. This is consistent with the finding reported here, *i.e.* the nitrido ligand exerts a stronger *trans*-influence than the oxo ligand.

Although the electronic influence of the nitrido ligand is greater than that of the oxo ligand there is apparently a larger steric requirement for the latter. Except in the rhenium complexes, this steric effect results in the metal atom in the oxo complexes being displaced to a greater degree from the basal plane than in the nitrido analogues and the O–M–L angles are generally greater than the N–M–L angles. This is surprising, since the very short M$\equiv$N bond lengths would cause a mutual repulsion between the nitrogen and basal ligands and hence a greater displacement of the metal atom from the basal plane.

It has been suggested that the *trans*-influence of the nitrido or oxo ligand may be attributed to either

TABLE VI. Comparative Structural Data for some Five-coordinate Complexes of the Type $[\mathrm{MX(L)_4}]^{n-}$ or $[\mathrm{MX(L{-}L)_2}]^{n-}$ (X = O or N)

$[\mathrm{MX(L)_4}]^{n-}$	M–X (Å)	M–L (Å)	X–M–L (°)	M–'sbp' (Å)	Reference
$\mathrm{(AsPh_4)_2[Tc^{V}N(dto)_2]}$	1.613(4)	2.387(1)	105.6(1)	0.647	this work
$\mathrm{(AsPh_4)[Tc^{V}O(dto)_2]}$	1.646(4)	2.329(1)	109.0(1)	0.759	this work
$\mathrm{(AsPh_4)[Tc^{VI}NCl_4]}$	1.581(5)	2.322(1)	103.34(3)	0.54	8
$\mathrm{[(N(PPh_3)_2][Tc^{V}OCl_4]}$	1.610(4)	2.31(1)	103.2–110.4	0.66	7
$\mathrm{(AsPh_4)[Re^{VI}NCl_4]}$	1.619(10)	2.322(2)	103.49(6)	0.545	25
$\mathrm{(AsPh_4)[Re^{V}OCl_4]}$	1.63(3)	2.344(4)	100.0(5)	0.407	26
$\mathrm{(AsPh_4)[Mo^{VI}NCl_4]}$	1.66(4)	2.345(5)	101.5(2)	0.47	27
$\mathrm{(AsPh_4)[Mo^{V}OCl_4]}$	1.71(3)	2.324(7)	104.6(2)	0.59	27
$\mathrm{(AsPh_4)[Mo^{V}OCl_4]}$	1.610(10)	2.333(3)	105.2(1)	0.61	28

'sbp' denotes the square basal plane.

electronic or steric effects [18]. Although the results presented here indicate that the two effects are not mutually exclusive, the results are difficult to rationalise. It is also interesting to note that differences in metal oxidation states in the complexes presented in Table VI cause no discernible changes in the structural parameters listed.

Supplementary Material

Anisotropic thermal parameters, hydrogen atom coordinates, short intermolecular contacts, listings of observed and calculated structure amplitudes and crystal packing diagrams are available from the authors on request. Stereodrawings of the complexes and perspective views of the cations in the complexes are also available.

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